

DEVELOPMENT OF DOPED NANOPOROUS CARBONS FOR HYDROGEN STORAGE (DE-FG26-06NT42675)

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ABSTRACT

OBJECTIVES

The objective of the project is to understand the active adsorption sites in carbon materials that have been activated with nanocatalysts, and use this knowledge to enhance synergistic effects that create new adsorption sites and activate the carbon nanomaterials for adsorption in the DOE target temperature and pressure range.

To understand, identify, and optimize specific adsorption sites, *in situ* high-pressure analytical techniques will be used to fully characterize these sites at the pressures of interest. We will combine multi-wavelength resonance Raman, infrared spectroscopy (IR), X-ray diffraction, and temperature programmed desorption (TPD) techniques with 100 bar measurements of overall adsorption uptake and energetics. Delineation of surface sites by factors such as their hybridization state, potential to (reversibly) rehybridize upon application of pressure, attached chemical functional groups, local bonding environment, and the nature of their binding to hydrogen, combined with adsorption measurements will lead to site specific structure composition relationships and optimization of material design based on this site specific knowledge.

ACCOMPLISHMENTS TO DATE

The overall research strategy is a three-pronged approach, including (1) materials synthesis, (2) materials characterization with *in situ* high pressure methods, and (3) high pressure measurements of hydrogen uptake and adsorption energies.

1. Materials Synthesis (Fonseca & Lueking). The theme of material synthesis is doped nanoporous carbons. Graphite nanofibers (GNF) and exfoliated graphite nanofibers (EGNF) will be used as the carbon support for doping, due to the ability to selectively tune the graphitic order (of GNF) and pore size (of EGNF). We have synthesized a suite of GNFs, varying the degree of graphitic order via catalyst selection and post-synthesis annealing. Currently, our GNF materials range from 40 to 100 Å in terms of crystallite size, as characterized by x-ray diffraction (XRD), and diameters less than 200 nm, as observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). We have optimized the yield during synthesis, such that we are now able to obtain uniform fibers with a typical yield of 90 g/g catalyst. We have also worked to vary the iron content of the material through variable-yield synthesis; this will serve as an alternate route to incorporate metals into the material for subsequent high-pressure measurements. EGNF have been synthesized via acid-intercalated and thermal treatment to modify the graphitic order and interplanar lattice spacing to range from 3.36 Å to 3.39 Å, characterized via XRD. Raman spectroscopy and TEM are also being used to characterize the materials. TEM and XRD are being utilized to characterize the particle size of doped-nanocarbons.

We are also using hydrogenated carbons, synthesized via reactive ball milling, to establish characterization procedures in Task 2. Reactive ball milling is suspected to lead to hydrogenated

tetrahedral amorphous carbon, with regions of sp^2 to sp^3 phase transition, based on previous work.¹ Therefore these materials provide a means to establish methods to study the carbon transitions that may occur during interaction with hydrogen.

2. Materials characterization with *in situ* high pressure methods (Schimmel & Badding). Multi-wavelength resonance micro-Raman spectroscopy is being used to characterize how much atomic hydrogen is chemically bonded to the carbon and the hybridization state (sp^2 vs sp^3) of the carbon. Currently, we are establishing procedures with carbon-based materials synthesized via reactive ball milling in a hydrogen donor solvent. These materials contain carbon, hydrogen, iron, and trace nickel, chromium, and other transition metals. At atmospheric conditions, the materials give rise to unique Raman vibrations that we are seeking to characterize in order to understand peaks that may arise in carbon-systems interacting with hydrogen. A peak at 4100-4200 cm^{-1} *may be* due to a perturbed Q branch vibration for molecular hydrogen or may be due to higher order carbon vibrations. The peak is dependent upon excitation wavelength, with an apparent resonance effect at 514 nm. The possibility of a molecular hydrogen peak at atmospheric pressure and temperature has not previously been observed, thus we are working to incorporate deuterated solvents into synthesis to conclusively assign the peak to either molecular hydrogen or carbon. If hydrogen, deuterium will shift the Raman vibration relative to hydrogen vibrations. A weak tetrahedral peak ('T' peak) at 900-1000 cm^{-1} may be used to track sp^3 -hybridized carbon; the relative intensity of this peak versus characteristic sp^2 peaks is being tracked via multi-wavelength Raman spectroscopy.

3. High pressure measurements of hydrogen uptake and adsorption energies (Lueking & Fonseca). We have been upgrading existing methods by which to measure hydrogen adsorption at high-pressure. A mass spectrometer is being integrated with an existing high-pressure gravimetric analyzer (IGA-003). A high-pressure differential volumetric apparatus is in the final stages of installation and calibration.

FUTURE WORK

The next step in materials synthesis is transition metal doping and characterization of the resulting metal-doped carbons. The characterization to date has been conducted at atmospheric pressure, and thus the next step is to utilize an existing diamond anvil cell for *in situ* measurements up to several 100 kbar. We are also considering the purchase of a sapphire cell for measurements at 100 bar. The differential volumetric apparatus is in the final stages of installation and calibration.

Ultimately, the research plan will incorporate a feedback loop to optimize the hydrogen uptake of the catalyzed carbon material by incorporating fundamental knowledge gained by the *in situ* high pressure measurements, and knowledge about site-specific structure composition relationships into synthesis of new materials.

LIST OF PAPER PUBLISHED, U.S. PATENT/PATENT APPLICATION(S), CONFERENCE PRESENTATIONS, AWARDS RECEIVED AS A RESULT OF SUPPORTED RESEARCH

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